Surface Tension Experimental Study for the Ternary System: 2-Amine-2-Methyl-1-Propanol+Diethanolamine+Water in the Temperature range 323.15-373.15 K in the full concentration range.

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Abstract

This work presents experimental orthobaric surface tension data for the three binaries and the ternary system formed by 2-Amine-2-Methyl-1-Propanol, Diethanolamine, and Water at six different temperatures (323.15, 333.15, 343.15, 353.15, 363.15 and 373.15 K) in the full concentration range. The experimental technique used for the measurement of surface tension was mainly the capillary rise method; for some determinations, the pendant drop method was also used. The determination of an experimental surface tension value, requires the corresponding density value so, density measurements were also carried out, using the vibrating tube method, for the binaries and ternary systems at 313.15, 323.15, and 333.15 K.

Using the experimental density data, excess volume values were derived for the same systems, which were correlated using the polynomial Redlich-Kister equation, adapted for ternary systems, incorporating a linear dependence with temperature into the corresponding adjustable parameters, which in turn were obtained by minimizing an objective function using the Gauss-Newton method.

Key words: Aqueous diethanolamine, aqueous 2-amine-2-methyl-1-propanol, surface tension, ternary mixture, density, excess volume.

Introduction.

In the oil industry, the presence of acid gases such as carbon dioxide (CO_2) and hydrogen sulfide (H_2S) in the production, transportation, and processing of hydrocarbon streams represents an important problem. Some of the industrial problems that arise due to the presence of these gases are corrosion, fouling and foaming in process and storage equipment. To prevent or abate these problems specialty chemicals have to be used together with separation processes, which commonly use aqueous alkanolamine solution as solvent. Our research group has been actively involved in the experimental and theoretical study of different thermophysical and phase equilibria properties related to the absorption of acid gases using the above mentioned solutions [1-7].

The knowledge of thermophysical and phase equilibria properties, related to the separation of acid gases from different hydrocarbon streams is of the utmost importance from a practical (process design, operation, and optimization) or scientific (for testing phase equilibria and thermophysical properties models) point of view. One of the thermophysical properties that plays an important role in most of the mass transfer operations is surface tension. Gas sweetening is carried out by putting in contact at countercurrent two streams, the hydrocarbon-rich gas and the aqueous alkanolamine solution, at a given temperature. Due to the presence of acidic (gases) and basic components (aqueous solution), this process involves a chemical acid-base reaction together with physical absorption. Surface properties of the gas-liquid system have to be taken into account to improve the mass transfer of the different components involved in the absorption process. The way surface

properties affect the performance of a given solvent has not been well established, however, the study of these properties for systems of industrial interest, which in most cases are multicomponent, is part of the current work of our research group in an attempt to understand the basic phenomena related to the absorption capacity and selectivity of mixtures of solvents.

In view of the above, we report in this work, experimental surface tension data for the binary systems 2-Amine-2-Methyl-1-Propanol(AMP) + Diethanolamine(DEA), AMP + Water, and DEA + Water, and also for the ternary system AMP+DEA+Water at six different temperatures (323.15, 333.15, 343.15, 353.15, 363.15, and 373.15 K). The experimental data were obtained using the well known capillary rise method. Furthermore, due to the need for density values, to derive the experimental surface tension data, those were also obtained at the following temperatures 313.15, 323.15, and 333.15 K, in the full concentration range, using the vibrating tube method. In order to easily handle the experimental density values, they were used to derive experimental excess volume data which in turn were correlated using a polynomial Redlich-Kister equation, adapted for ternary systems, and incorporating a linear dependence with temperature into the corresponding adjustable parameters.

Experimental Section

To obtain the experimental surface tension data two different techniques were used: the very well-known capillary rise method [3,4], which is considered to be one of the most

accurate absolute methods to determine surface tension [8], and the pendant drop method, for which, a commercial First Ten Amgstrons (FTA) experimental device was employed. The temperature control for surface tension determinations was ±0.002 K using the capillary rise method, and ±0.1 K for the case of the pendant drop method. The experimental errors obtained for the surface tension determinations were 0.05 mNm^{-1} and 0.25 mNm^{-1} for the capillary rise and pendant drop methods, respectively.

Purity of substances and mixture preparation

The Diethanolamine was from J.T. Baker which was distilled and its purity was established by gas chromatography obtaining 99% in area, the 2-Amine-2-Methyl-1-Propanol was from Aldrich, it was also distilled reaching 99.3% in area by gas chromatography, water was twice distilled and deionized. Mixtures were prepared by weight using an analytic Sartorius balance with a precision and accuracy of ±0.0001g, with which an error of ±0.0001 in mole fraction is obtained for the concentration of the mixtures.

Results

Experimental density-excess volume data.

The experimental density values for the pure substances, binary, and ternary mixtures were determined using a vibrating-tube Sodev densitometer. The experimental density values

were used to derive values of the molar excess volume, which in turn were used to carry out a correlation with a polynomial Redlich-Kister equation adapted for ternary systems and incorporating a linear dependence with temperature for the corresponding adjustable parameters. Details of the correlation, equations and methodology, can be found in another work from our laboratory accepted also for presentation at the 14th International Symposium on Thermophysical Properties [7].

For the correlation of the experimental excess volume values, 253 data points were used to adjust the 18 parameters of the polynomial Redlich-Kister equation, some of the experimental data were taken from literature [7-15], and some other were measured during the development of the present work. The parameters obtained for the ternary system are summarized in Table 1.

To establish the quality of the correlation with the parameters from Table 1, excess volume and density values were derived in order to carry out a comparison with 139 data points reported in literature. It has to be mentioned that these points were not included in the correlation. In fact, most of these 139 points are at a different temperature and concentration than those used to adjust the parameters of the polynomial Redlich-Kister equation, which means that our correlation can be useful to carry out extrapolations. The absolute average difference obtained from the comparison of experimental and calculated density values was 0.0015 g cm^{-3}, which can be interpreted as an indicator of the goodness of the correlation. From an error analysis on the equation used to derive surface tension with the capillary rise method, which includes density value, a variation of ±0.001 g cm^{-3} in

density corresponds to a variation of ±0.01 *m*N m^{-1} in the corresponding surface tension value, which is within the error reported for our surface tension measurements. The correlation scheme used for the molar excess volume values is able to reproduce the concentration and temperature dependence of the experimental density values to a high degree of reliability.

Experimental surface tension results.

In view of the use of two experimental techniques, the capillary rise and the pendant drop, to determine the surface tension for the binaries and ternary systems reported in this work, we have carried out a comparison of our results with literature data. In Figure 1 there are included experimental results for the binaries AMP + H2O and DEA + H2O at 323.15 K, for which González et al. [16, 17] have reported surface tension values. The Figure also includes experimental surface tension values obtained in our Laboratory for the same systems, at the same temperature, these data were obtained using the two different experimental techniques above mentioned. As can be observed from Figure 1, the experimental values obtained in our Laboratory using two different experimental techniques, are highly consistent among themselves. The deviations observed between the experimental results from this work and those reported in literature, which are about 3 and 4 mNm^{-1} for both systems above 0.1 in alkanolamine mole fraction, respectively, could be due to different factors including purity of substances, sample preparation, and the experimental technique used. In view of these curves, it seems that a possible explanation

could correspond to sample evaporation (mainly water evaporation), which reduces the experimental surface tension value.

Figures 2-4 include experimental surface tension values for the three possible binaries of the ternary system AMP + DEA + H_2O at different temperatures between 323 and 373.15 K. From these figures it is possible to observe the difference in water surface tension abatement by the addition of one alkanolamine (AMP or DEA), the binary aqueous system with AMP shows a higher decay in surface tension even at very low alkanolamine concentration, just for comparison, at T= 323.15 K, and xAMP = 0.1 the surface tension is approximately 42 mN m^{-1} whereas at the same concentration, the system with DEA shows a surface tension value near 55 mN m^{-1}.

Table 2 presents experimental surface tension and density values for the ternary system studied in this work, AMP + DEA + Water, at 323. 15 K. The experimental surface tension values included in this table were obtained using the pendant drop method. As can be observed from this table, all of them correspond to mixtures with high water content. These experimental surface tension values were obtained to complement those measured with the capillary rise method. The density values included in Table 2 were derived using the Redlich-Kister polynomial equation, as mentioned previously.

Table 3 shows similar experimental surface tension and density values for the same ternary system, AMP + DEA + Water, at 323.15 K, the difference with the information included in Table 2 is that the surface tension information included in Table 3 was obtained using the

capillary rise method. Density values included in this table were obtained as described previously. In this Table there are two sets of data grouped in two blocks of four columns each; in which the mole fraction of the two alkanolamines, the surface tension and density values are included. The first block on the left hand side presents experimental surface tension and density values for the pure components and the binaries of this ternary system, whereas the second block presents the same type of information for the ternary system.

Figures 5 and 6 show two perspectives of a graphical representation of the experimental surface tension data presented separately in Tables 2 and 3 for the binary and ternary systems. These experimental values are presented in a three-axis coordinate system. The geometric form of the graph allows to mantain the triangular concentration coordinates of a ternary system for which the base of the triangular prism is used. The vertical axis is used to represent the surface tension values. The vertical axis is plotted in a normalized scale taken as maximum and minimum values those corresponding to the pure components with the higher and lower surface tension, water and AMP, respectively, which permits to plot the normalized surface tension value between 0 and 1. This normalization is carried out to take advantage of the height of the prism to visualize the experimental points. In Figures 5 and 6 it is possible to observe the spatial distribution of the experimental surface tension values for the different concentrations of the ternary system studied, including the corresponding binaries and pure components. From these figures it is possible to highlight the experimental trends showed by the three different binaries. For the case of the two aqueous binaries, the higher decay in surface tension occurs for the system with AMP, which could be part of a possible explanation for its larger absorption capacity and

selectivity towards acid gases than aqueous solutions of DEA. The experimental behavior showed by the experimental points inside the ternary concentration zone follows that corresponding to the delimiting binaries, that is, the experimental points are distributed on an imaginary surface delimited by the surface tension-concentration curves of the three binary systems conforming the ternary under study.

Experimental surface tension and density values were also obtained for the same ternary system at five different temperatures: 333.15, 343.15, 353.15, 363.15, and 373.15 K, in the full concentration range. Unfortunately, due to space limitations, the corresponding experimental values are not included in this work, but will be part of a publication.

Conclusions

The experimental surface tension and density data included in this work for the binaries and ternary systems formed by AMP, DEA, and Water, are of high quality, according to the internal comparison carried out for surface tension using two different experimental techniques, and that made using experimental data from literature

The density values, derived in this work are sufficiently reliable, according to the corresponding error analysis, for the purposes of determining experimental surface tension values.

In view of the scarcity of experimental thermophysical properties for systems with three or more components, this work represents a contribution towards understanding the experimental behavior of systems that are relevant for a given industrial process, as is the case of surface properties of solvents used in gas sweetening.

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Table 1.Values of the adjustable parameters of the Redlich-Kister polynomial equation used to correlate experimental excess volume data for the ternary system AMP + DEA + Water in the full concentration range at different temperatures.

A_{00}	A_{01}	A_{10}	A_{11}	A_{20}	A_{21}
-1.48701E1	4.158318E-2	4.634566	-1.015822E-2	-1.213465E3	3.749824
B_{00}	B_{01}	B_{10}	B_{11}	B_{20}	B_{21}
-3.984621E1	1.13504E-1	-8.85866E1	2.914903E-1	-6.159371E1	1.970868E-1
C_{00}	C_{01}	C_{10}	C_{11}	C_{20}	C_{21}
-3.557594	4.190492E-3	9.213049E-1	9.684273E-4	-2.506058	8.27562E-3

The standar deviation of the correlation was 0.074 cm^3 mol^{-1}.

Table 2 Experimental results of surface tension for the ternary system AMP+DEA+H_2O, at 323.15 K, using the pendant drop method.

*x*AMP	*x*DEA	σ *m*Nm^{-1}	ρ g cm^{-3}
0.0514	0.1492	48.14	1.03333
0.0796	0.1198	45.20	1.02149
0.0993	0.0997	43.69	1.01313
0.1200	0.0793	41.95	1.00438
0.1501	0.0504	40.74	0.99166
0.0295	0.0705	51.49	1.01739
0.0390	0.0592	49.59	1.01183
0.0509	0.0493	47.90	1.00632
0.0599	0.0395	46.71	1.00127
0.0696	0.0289	45.98	0.99574

Tabla 3. Experimental results of surface tension for the ternary system AMP+DEA+H_2O in the full concentration range, at 323.15 K, using the capillary rise method.

*x*AMP	*x*DEA	σ mNm^{-1}	ρ g cm^{-3}	*x*AMP	*x*DEA	σ mNm^{-1}	ρ g cm^{-3}
1.0000	0.0000	30.41	0.90968	0.1009	0.7967	43.47	1.06199
0.0000	1.0000	47.01	1.07776	0.2009	0.6909	42.36	1.04462
0.0000	0.0000	68.46	0.98805	0.2997	0.5979	39.88	1.02664
0.1390	0.8610	42.76	1.05860	0.2992	0.5954	39.91	1.02657
0.1583	0.8417	42.34	1.05561	0.3986	0.4972	38.85	1.00761
0.3035	0.6965	39.50	1.03157	0.5003	0.3984	35.30	0.98811
0.4300	0.5700	37.15	1.00949	0.5967	0.2990	36.21	0.96896
0.5398	0.4609	35.65	0.99027	0.6897	0.1974	34.57	0.94947
0.6996	0.3004	33.33	0.96241	0.7973	0.1013	32.89	0.92964
0.8173	0.1827	32.52	0.94208	0.1005	0.7021	44.58	1.05994
0.9147	0.0853	31.31	0.92504	0.1989	0.5965	41.79	1.04112
0.0100	0.0000	64.03	0.98743	0.2992	0.4982	39.62	1.02089
0.0226	0.0000	51.20	0.98658	0.3986	0.3995	35.90	1.00005
0.0838	0.0000	42.03	0.98153	0.4991	0.2996	34.70	0.97852
0.1159	0.0000	41.75	0.97843	0.5968	0.1998	33.67	0.95692
0.2323	0.0000	36.61	0.96562	0.7035	0.0993	31.92	0.93407
0.2852	0.0000	35.78	0.95938	0.0996	0.5964	44.50	1.05744
0.3916	0.0000	34.45	0.94680	0.2006	0.4994	41.30	1.03640
0.5140	0.0000	33.18	0.93325	0.2986	0.3975	39.92	1.01422
0.6452	0.0000	31.96	0.92108	0.3982	0.2998	37.54	0.99116
0.7590	0.0000	31.30	0.91342	0.4982	0.1993	36.10	0.96713
0.0000	0.0191	63.16	0.99951	0.5969	0.1000	33.46	0.94271
0.0000	0.0497	59.56	1.01447	0.0999	0.4988	44.57	1.05423
0.0000	0.1230	56.53	1.03861	0.1982	0.3971	41.36	1.03098
0.0000	0.1939	54.06	1.05266	0.3004	0.2926	40.08	1.00491
0.0000	0.2846	52.67	1.06339	0.3994	0.1992	36.03	0.97989
0.0000	0.4054	51.16	1.07088	0.4991	0.1005	34.89	0.95311
0.0000	0.5875	49.04	1.0753	0.0997	0.3994	45.67	1.04970
0.0000	0.6720	48.33	1.07608	0.2005	0.2993	41.86	1.02305
0.0000	0.8979	47.21	1.07712	0.3971	0.1016	34.23	0.96620
				0.1001	0.3004	43.42	1.04273
				0.1991	0.1999	39.87	1.01243
				0.3000	0.1003	36.75	0.97996
				0.1002	0.2004	43.93	1.03163
				0.1999	0.1005	40.52	0.99588
				0.0997	0.0998	43.08	1.01308

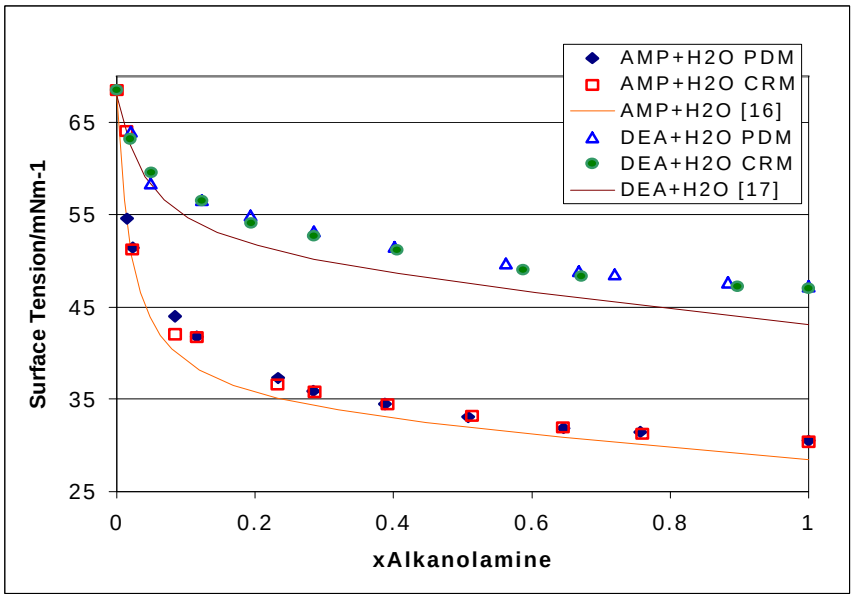

Figure 1. Experimental surface tension data for the binary systems AMP + Water and DEA + Water, at 323.15 K. Points; data from this work with the Pendant Drop (PDM), Capillary Rise Methods (CRM). Full curves, data from the literature.

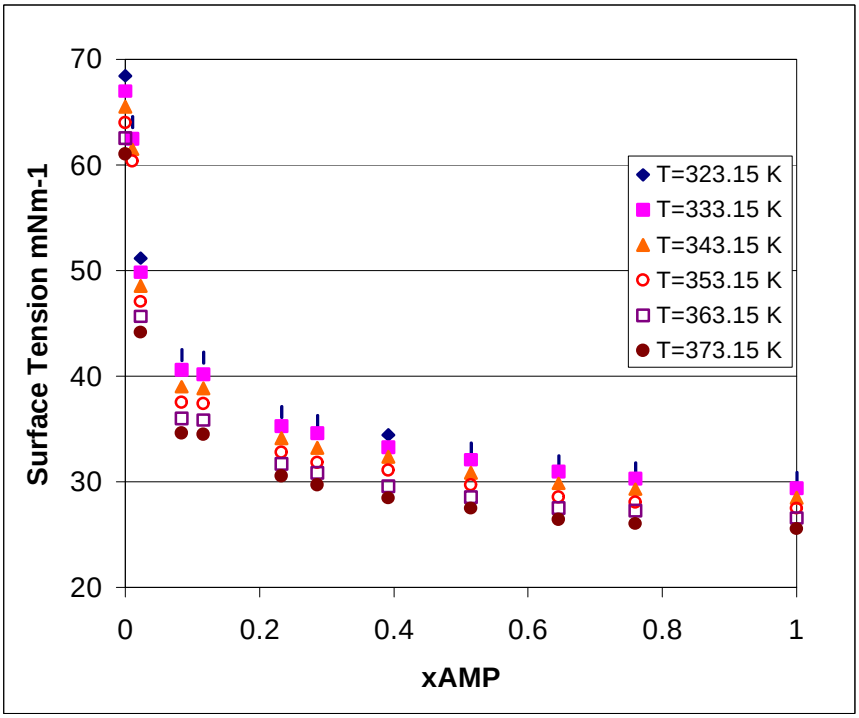

Figure 2. Experimental surface tension data as a function of alkanolamine concentration for the binary system AMP+H2O, at several temperatures

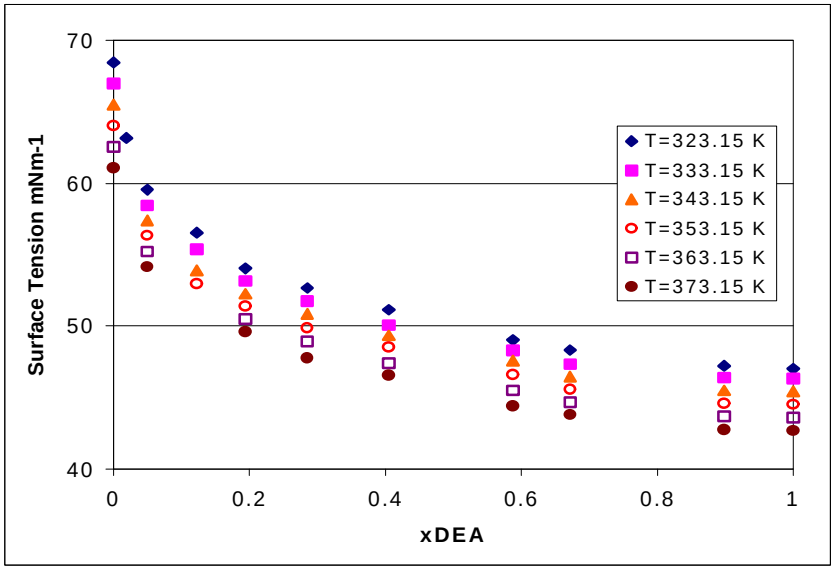

Figure 3. Experimental surface tension data as a function of alkanolamine concentration for the binary system DEA+H2O, at several temperatures

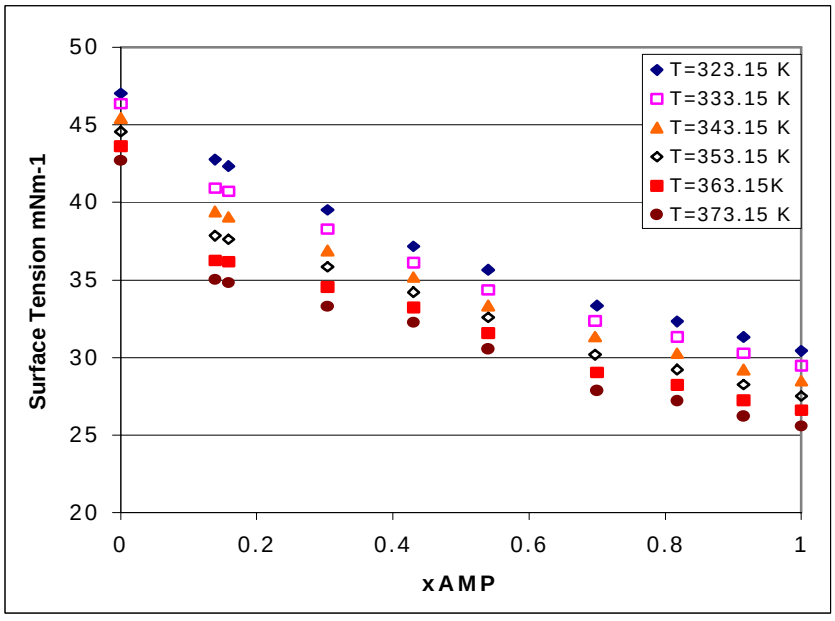

Figure 4. Experimental surface tension data as a function of alkanolamine concentration for the binary system AMP + DEA, at several temperatures

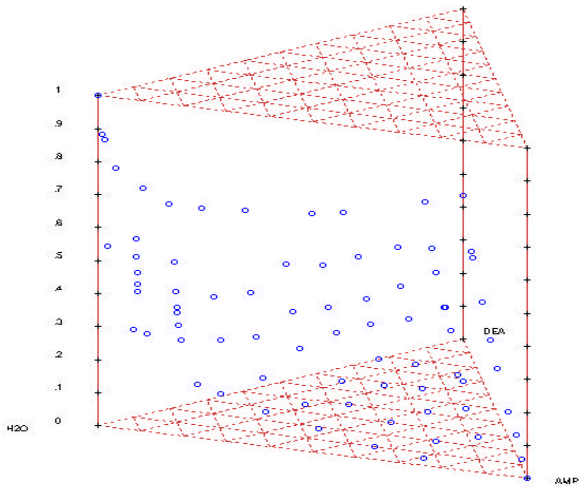

Figure 5. Experimental surface tension data for the ternary system AMP + DEA + Water at 323.15 K.

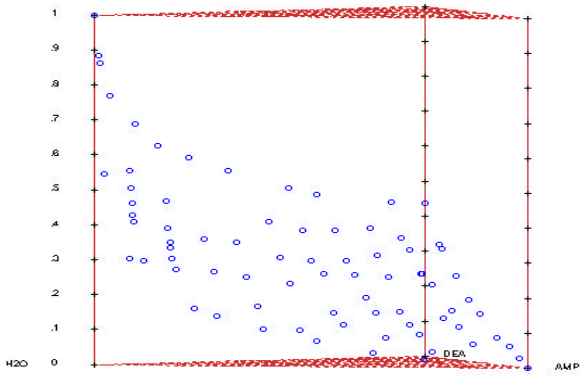

Figure 6. Experimental surface tension data for the ternary system AMP + DEA + Water at 323.15 K.